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(54) Title: IMPACT MODIFIED POLYPHENYLENE ETHER-POLYAMIDE COMPOSITIONS (57) Abstract <p>Thermoplastic compositions comprised of compatible combinations of a polyphenylene ether resin and a polyamide resin which require improved low temperature ductility can be impact modified with a modifying agent comprising a partially hydrogenated diblock copolymer of styrene and ethylene/propylene.</p>		

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IMPACT MODIFIED POLYPHENYLENE ETHER-
POLYAMIDE COMPOSITIONS

Cross-Reference to Related Application

This application is a Continuation-In-Part of
5 copending application Serial No. 837,474; filed
March 7, 1986, and incorporated herein by reference.

Field of the Invention

Compositions comprising a combination of
polyphenylene ether resin and polyamide resin can be
10 impact modified with a selectively hydrogenated diblock
copolymer of styrene and ethylene/propylene which is
particularly effective for thermoplastic applications
requiring improved low temperature ductility.

Background of the Invention

15 Polyphenylene ether resins have been modified with
polyamide resins to provide a wide variety of
beneficial properties such as excellent heat
resistance, chemical resistance, impact strength,
hydrolytic stability and dimensional stability.

20 The improved properties of polyphenylene
ether-polyamide compositions have found great utility
in thermoplastic applications which take advantage of
such properties. For example, exterior automotive
applications such as body panels and wheel covers can
25 benefit from the improved thermal properties of
polyphenylene ether-polyamide compositions (PPE/PA
compositions). In a typical automotive application such
as a fender part, a thermoplastic must be capable of
providing satisfactory properties over a wide range of
30 end-use temperatures.

Although many important thermoplastic applications
for PPE/PA compositions require that the resin be

- 2 -

impact modified to provide adequate performance, the ductile behavior of such reasons is often overlooked.

Ductile behavior is an important physical property for thermoplastics in many applications, and particularly for automotive parts which may experience extremely rigorous conditions at very low temperatures. The mode of failure for a molded part, whether ductile or brittle failure, at a given temperature is also an important indication of the utility of the thermoplastic. Improvements in low temperature ductile-brittle transitions will increase the opportunity for polyphenylene ether-polyamide compositions to adequately perform in thermoplastic applications where such properties are required or desired. Many conventionally modified thermoplastics offer advantages and disadvantages but do not provide the range of ductile behavior improvement offered by compositions of the present invention. Conventional impact modifiers for polyphenylene ether-polyamide compositions are ineffective in this regard compared to the impact modification system described herein.

It has now been discovered that polyphenylene ether-polyamide compositions can be improved by combining the base resin with a modifier comprised of a partially hydrogenated diblock copolymer of styrene and ethylene-propylene in accordance with the description below. Such compositions exhibit the superior properties normally associated with compatible polyphenylene ether/polyamide compositions as well as unexpectedly improved ductile behavior.

- 3 -

SUMMARY OF THE INVENTION

Thermoplastic compositions of the present invention are comprised of:

a. a base resin which is a compatibilized combination of a polyphenylene ether resin and a polyamide resin; and

b. an amount of an impact modifying agent effective for improving the ductile behavior of such base resin and which is a selectively hydrogenated diblock copolymer of styrene and ethylene/propylene.

Preferred reinforced grades of compatibilized polyphenylene ether-polyamide resin blends will additionally contain, as component (c.), about 5 to 45 weight percent of chopped glass fiber, based upon the weight of components a., b., and c. taken together.

Preferred polyphenylene ether resins and polyamide resins as well as means for providing compatibilized combinations thereof are described below.

In general it is desirable that the polyamide component comprise a continuous phase in the overall composition and, therefore, typically at least 35 percent by weight of the total PPE-polyamide-modifier composition will be comprised of the polyamide component. The remainder of the composition will be comprised of the PPE and diblock copolymer modifier, in typical weight ratios described below.

The preferred diblock modifying component is typically comprised of 20 to 40 weight percent of a styrene block and 80 to 60 weight percent of an ethylene/propylene block which can be derived from a rubbery block which has been selectively hydrogenated to eliminate some or all of the residual unsaturation contained in the rubbery block.

- 3.1 -

Glass reinforced grades of compatibilized polyphenylene ether-polyamide resin compositions are extremely important in thermoplastic applications requiring a unique combination of physical properties such as impact strength, rigidity and modulus, dimensional stability, high heat resistance as well as chemical resistance. Glass reinforced compositions of the present invention would not be expected to exhibit the improved ductile response seen in non-reinforced compositions, nonetheless, glass filled resins will benefit from the incorporation of the aforementioned selectively hydrogenated diblock copolymer in several ways. Principally, glass filled PPE-polyamide compositions of the present invention offer good physical properties. Surprisingly, however, glass reinforced compositions containing the diblock copolymer also retain important physical properties to a greater degree upon heat aging, an important consideration for many thermoplastic applications. Then to thirty weight percent loadings of chopped glass fiber can typically be utilized to advantage in these compositions. These weight percents would be based upon the weight of the polyphenylene ether resin, the polyamide resin, the impact modifier and the glass, taken together. More or less glass (e.g. 5 to 45 weight percent) can also be utilized in certain circumstances. Less than about 5 parts glass begins to perform like an unreinforced product. More than about 45 weight percent glass begins to interfere with the ability of the resin to coat and bind the glass effectively.

- 4 -

Description of the Invention

Polyphenylene ethers are a well known class of compounds sometimes referred to as polyphenylene oxides. Examples of suitable polyphenylene ethers and processes for preparation can be found in U.S Patent Nos. 3,306,874; 3,306,875; 3,257,357; and 3,257,358 which are each incorporated by reference. Compositions of the present invention will encompass homopolymers, copolymers and graft copolymers obtained by the oxidative coupling of phenolic compounds. The preferred polyphenylene ethers used as base resins in compositions of the present invention will be comprised of units derived from 2,6-dimethyl phenol. Also contemplated are PPE copolymers comprised of units derived from 2,6-dimethyl phenol and 2,3,6-trimethyl phenol.

A particularly useful polyphenylene ether would be poly(2,6-dimethyl-1,4-phenylene ether) having an intrinsic viscosity (I.V.) greater than, approximately 0.10 dl/g as measured in chloroform at 25°C. The I.V. will typically be between 0.30 and 0.50 dl/g.

The polyamide resins useful in the practice of the present invention are a generic family of resins known as nylons, characterized by the presence of an amide group (-CONH-). Nylon-6 and nylon-6,6 are the generally preferred polyamides and are available from a variety of commercial sources. Other polyamides, however, such as nylon-4, nylon-12, nylon-6,10, nylon-6,9 or others such as the amorphous nylons may be useful for particular polyphenylene ether-polyamide applications.

The polyamides can be provided by a number of well known processes. Nylon-6, for example, is a

- 5 -

polymerization product of caprolactam. Nylon-6,6 is a condensation product of adipic acid and hexamethylenediamine. A nylon-6,6 having an average molecular weight of approximately 10,000 is especially preferred for many useful polyphenylene ether-polyamide thermoplastic applications. Preferred polyamides will typically have a relative viscosity of at least 35, in accordance with ASTM Test Method D789.

In U.S. Patent 3,379,792, (incorporated herein by reference) Finholt provided useful combinations of polyphenylene ether and polyamide, where the weight percent of the polyamide component did not exceed about 25 percent. Beyond that proportion, noticeable decrease in properties was attributed to the relative incompatibility of the two resins.

In preferred embodiments of the present invention, a compatibilizing agent may be employed in the preparation of the composition. The two-fold purpose for using compatibilizing agents is to improve, in general, the physical properties of the polyphenylene ether-polyamide resin, as well as to enable the use of a greater proportion of the polyamide component. When used herein, the expression "compatibilizing agent" refers to those polyfunctional compounds which interact with either the polyphenylene ether, the polyamide or both. This interaction may be chemical (e.g. grafting) or physical (e.g. affecting the surface characteristics of the dispersed phases). In either instance the resulting polyphenylene ether-polyamide composition appears to exhibit improved compatibility, particularly as evidenced by enhanced impact strength, mold knit line strength and/or elongation. As used herein, the expression "compatibilized polyphenylene

- 6 -

ether-polyamide base resin" refers to those compositions which have been physically or chemically compatibilized with an agent as discussed above, as well as those compositions which are physically compatible without such agents, as taught in the Finholt patent mentioned earlier.

Examples of the various compatibilizing agents that may be employed in the practice of the present invention include: a) liquid diene polymers, b) epoxy compounds, c) oxidized polyolefin wax, d) quinones, e) organosilane compounds and f) polyfunctional compounds as described hereinafter.

Liquid diene polymers (a) suitable for use herein include homopolymers of a conjugated diene with at least one monomer selected from the group consisting of other conjugated dienes; vinyl monomer, e.g. styrene and alpha-methyl styrene; olefins, e.g. ethylene, propylene, butene-1, isobutylene, hexene-1, octene-1 and dodecene-1, and mixtures thereof, having a number average molecular weight of from 150 to 10,000 preferably 150 to 5,000. These homopolymers and copolymers can be produced by the methods described in, for example, U.S. Patent Nos. 4,054,612; 3,876,721 and 3,428,699 incorporated herein by reference and include, among others, polybutadiene, polyisoprene, poly(1,3-pentadiene), poly(butadiene-isoprene), poly(styrene-butadiene), polychloroprene, poly(butadiene-alpha methylstyrene), poly(butadiene-styrene-isoprene), poly(butylene-butadiene) and the like.

Epoxy compounds (b) suitable for use in the practice of the present invention include: (1) epoxy resins produced by condensing polyhydric phenols (e.g.

- 7 -

bisphenol-A, tetrabromobisphenol-A, resorcinol and hydroquinone) and epichlorohydrin; (2) epoxy resins produced by condensing polyhydric alcohols (e.g. ethylene glycol, propylene glycol, butylene glycol, 5 polyethylene glycol, polypropylene glycol, pentaerythritol and trimethylolethane and the like) and epichlorohydrin; (3) glycidyletherified products of monohydric alcohols and monohydric phenols including phenyl glycidylether, butyl glycidyl ether and cresyl 10 glycidylether; (4) glycidyl derivatives of amino compounds for example, the diglycidyl derivative of aniline, and (5) epoxidized products of higher olefinic or cycloalkene, or natural unsaturated oils (e.g. soybean) as well as of the foregoing liquid diene 15 polymers.

Oxidized polyolefin waxes (c) are well known and a description thereof and processes for the production of the same are found in U.S. Patent Nos. 3,822,227 and 3,756,999 and German Patent Publications 3,047,915 and 202,201,862, herein incorporated by reference.

Generally, these are prepared by an oxidation or suspension oxidation of polyolefin. An especially preferred polyolefin wax is "Hoechst Wacks".

Quinone compounds (d) suitable for use herein are 25 characterized as having in the molecule of the unsubstituted derivative at least one 6 membered carbon ring; at least two carbonyl groups in the ring structure, both of which may be in the same or, if more than one ring, different rings, provided that they 30 occupy positions corresponding to the 1,2- or 1,4-orientation of the monocyclic quinone; and at least two carbon-carbon double bonds in the ring structure, said carbon-carbon double bonds and carbonyl carbon-oxygen

- 8 -

double bonds being conjugated with respect to each other. Where more than one ring is present in the unsubstituted quinone, the rings may be fused, non-fused or both: non-fused rings may be bound by a
5 direct carbon-carbon double bond or by a hydrocarbon radical having conjugated unsaturation such as $=C-C=$.

Substituted quinones are also within the scope of the present invention. The degree of substitution; where substitution is desired, may be from one to the
10 maximum number of replaceable hydrogen atoms.

Exemplary of the various substituents that may be present on the unsubstituted quinone structures include halogen, e.g. chlorine, bromine, flourine, etc., hydrocarbon radicals including branched and unbranched,
15 saturated and unsaturated alkyl, aryl, alkyl aryl and cycloalkyl radicals and halogenated derivatives thereof; and similar hydrocarbons having hetero atoms therein, particularly oxygen, sulfur or phosphorous and wherein the same connects the radical to the quionone
20 ring (e.g. oxygen link).

Exemplary of the various quinones there may be given 1,2- and 1,4-benzoquinone; 2,6-diphenyl quionone; tetramethyldiquinone; 2,2'- and 4,4'-diphenoquinone; 1,2-, 1,4- and 2,6-naphthoquinone; chloranils;
25 2-chloro-1,4-benzoquinone; 2,6-dimethyl benzoquinone and the like.

Organosilane compounds (e) suitable as compatibilizing agents are characterized as having in the molecule (a) at least one silicon atom bonded to a
30 carbon through an oxygen link and (b) at least one carbon-carbon double bond or carbon-carbon triple bond and/or a functional group selected from the group consisting of an amine group or a mercapto group

- 9 -

provided that the functional group is not directly bonded to the silicon atom.

In such compounds, the C-O-Si component is generally present as an alkoxyl or acetoxy group bonded directly to the silicon atom, wherein the alkoxyl or acetoxy group generally has less than 15 carbon atoms and may also contain hetero atoms (e.g. oxygen). Additionally, there may also be more than one silicon atom in the compound, such multiple silicon atoms, if present, being linked through an oxygen link (e.g. siloxanes), a silicon-silicon bond; or a bifunctional organic radical (e.g. methylene or phenylene groups).

Examples of suitable organosilane compounds include: gamma amino propyltriethoxy silane, 2-(3-cyclohexenyl)ethyl trimethoxy silane; 1,3-divinyl tetraethoxy silane; vinyl tris-(2-methoxyethoxy)silane; 5-bicycloheptenyl)triethoxy silane and gamma mercapto propyl trimethoxy silane.

Finally, polyfunctional compounds (f) which may be employed as compatibilizer in the practice of the present invention are of three types. The first type of polyfunctional compounds are those having in the molecule both (a) a carbon-carbon double bond or a carbon-carbon triple bond and (b) at least one carboxylic acid, acid anhydride, acid halide, anhydride, acid halide anhydride, acid amide, acid ester, imide, amino, or hydroxy group. Examples of such polyfunctional compounds include maleic acid; maleic anhydride; fumaric acid; citraconic acid; itaconic acid; maleimide; maleic hydrazide; reaction products resulting from a diamine and maleic anhydride, maleic acid, fumaric acid, etc; dicholoro maleic anhydride; maleic acid amide; unsaturated dicarboxylic

- 10 -

acids (e.g. acrylic acid, butenoic acid, methacrylic acid, t-ethylacrylic acid, pentenoic acid); decenoic acids, undecenoic acids, dodecenoic acids, linoleic acid, etc.); esters, acid amides or anhydrides of the foregoing unsaturated carboxylic acids; unsaturated alcohols (e.g. allyl alcohol, crotyl alcohol, methyl vinyl carbinol, 4-pentene-1-ol, 1,4-hexadiene-3-ol, 3-butene-1,4-diol, 2,5-dimethyl-3-hexene-2,5-diol and alcohols of the formulae $C_nH_{2n-5}OH$, $C_nH_{2n-7}OH$ and $C_nH_{2n-9}OH$, wherein n is a positive integer up to 30), unsaturated amines resulting from replacing the -OH group(s) of the above unsaturated alcohols with NH_2 groups; and functionalized diene polymers and copolymers. Of these, one of the preferred compatibilizing agents for compositions of the present invention is maleic anhydride.

The second group of polyfunctional compatibilizer compounds suitable for use herein are characterized as having both (a) a group represented by the formula (OR) wherein R is hydrogen or an alkyl, aryl, acyl or carbonyl dioxy group and (b) at least two groups each of which may be the same or different selected from carboxylic acid, acid halide, acid anhydride, anhydride, acid halide anhydride, acid ester, acid amide, imido, amino and salts thereof. Typical of this group of compatibilizers are the aliphatic polycarboxylic acids, acid esters and acid amides represented by the formula:

$$(R^I O)_m R (COOR^{II})_n (CONR^{III} R^{IV})_s$$
 wherein R is a linear or branched chain, saturated aliphatic hydrocarbon of from 2 to 20, preferably 2 to 10, carbon atoms; R^I is selected from the group

- 11 -

consisting of hydrogen or an alyl, aryl, acyl or carbonyl dioxy group of 1 to 10, preferably 1 to 6, most preferably 1 to 4, carbon atoms, especially preferred is hydrogen; each R^{II} is independently
5 selected from the group consisting of hydrogen or an alkyl or aryl group of from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms; each R^{III} and R^{IV} is independently selected from the group consisting essentially of hydrogen or an alkyl or aryl group of
10 from 1 to 10, preferably from 1 to 6, most preferably 1 to 4, carbon atoms; m is equal to 1 and (n + s) is greater than or equal to 2, preferably equal to 2 or 3, and n and s are each greater than or equal to zero and wherein (OR^I) is alpha or beta to a carbonyl group and
15 at least two carbonyl groups are separated by 2 to 6 carbon atoms. Obviously, R^I , R^{II} , R^{III} and R^{IV} cannot be aryl when the respective substituent has less than 6 carbon atoms.

Illustrative of suitable polycarboxylic acids
20 there may be given citric acid, malic acid, and agaricic acid; including the various commercial forms thereof, such as, for example, the anhydrous and hydrated acids. Of these, citric acid is another of the preferred compatibilizing agents. Illustrative of
25 acid esters useful herein include for example, acetyl citrate and mono- and/or di- stearyl citrates and the like. Suitable acid amides useful herein include for example N,N'- diethyl citric acid amide; N,N'-dipropyl citric acid amide; N-phenyl citric acid amide;
30 N-dodecyl citric acid amide; N,N'-didodecyl citric acid amide and N-dodecyl malic acid amide. Derivatives of the foregoing polycarboxylic acids are also suitable for use in the practice of the present invention.

- 12 -

Especially preferred derivatives are the salts thereof, including the salts with amines and/preferably, the alkali and alkaline metal salts. Exemplary of suitable salts include calcium malate, calcium citrate,

5 potassium malate and potassium citrate.

The third group of polyfunctional compatibilizer compounds suitable for use herein are characterized as having in the molecule both (a) an acid halide group, most preferably an acid chloride group and (b) at least
10 one carboxylic acid, carboxylic acid anhydride, acid ester or acid amide group, preferably a carboxylic acid or carboxylic acid anhydride group. Exemplary of compatibilizers within this group there may be given
15 trimellitic anhydride acid chloride, chloroformyl succinic anhydride, chloro formyl succinic acid, chloroformyl glutaric anhydride, chloroformyl glutaric acid, chloroacetyl succinic anhydride, chloroacetylsuccinic acid, trimellitic acid chloride and chloroacetyl glutaric acid. Among these,
20 trimellitic anhydride acid chloride is preferred. Furthermore, it is especially preferred that compatibilizers of this group be prereacted with at least a portion of the polyphenylene ether whereby the compatibilizing agent is a PPE-functionalized compound.

25 Each of the foregoing compatibilizing agents are more fully described in U.S. Patent Nos. 4,315,086 and 4,642,358; U.S. Patent Applications Serial Nos. 669,130; 736,489 and 780,151 filed November 7, 1984, May 20, 1985, and, September 26, 1984, respectively,
30 and European Patent Application No. 04640, altogether herein incorporated by reference.

The foregoing compatibilizing agents may be used alone or in any combination of one another.

- 13 -

Furthermore, they may be added directly to the melt blend or precompounded with either or both the polyphenylene oxide and polyamide as well as with other resinous materials employed in the preparation of the compositions of the present invention. With many of the foregoing compatibilizing agents, particularly the polyfunctional compounds, even greater improvement in compatibility is found where at least a portion of the compatibilizing agent is precompounded with all or part of the polyphenylene oxide. It is believed that such precompounding may cause the compatibilizing agent to react with the polymer and, consequently, functionalize that polymer. as noted above for example, the polyphenylene oxide may be precompounded with trimellitic anhydride acid chloride to form an anhydride functionalized polyphenylene ether which has improved compatibility with the polyamide compared to a non-functionalized polyphenylene ether.

Where the compatibilizing agent is employed in the preparation of the compositions of the present invention, the initial amount used will be dependent upon the specific compatibilizing agent chosen and the specific polymeric system to which it is added. The examples below depict several suitable compatibilization methods used in the practice of the present invention.

Those skilled in the art will be able to provide impact improved compositions comprising various proportions of the polyphenylene ether resin, the polyamide resin, the compatibilizing agent, if required, and the diblock copolymer impact modifier. In general, however, where chemical resistance is a desirable property of the thermoplastic resin, it will

- 14 -

ordinarily be necessary that the polyamide resin form a continuous phase of the resin composition. Therefore, to avoid a phase inversion whereby the polyamide phase is discontinuous, the preferred compositions of the present invention will be comprised of a polyamide resin in an amount equal to or greater than approximately 35 percent by weight of the total composition (i.e. the PPE, PA, and diblock copolymer components taken together). The remaining components will be comprised of the PPE and diblock copolymer impact modifier, and may together account for up to approximately 65 percent by weight of the total resinous components of the composition.

A variety of useful polyphenylene ether-polyamide compositions can be provided which include varying amounts of the diblock copolymer modifying agent. Typically, improved properties, especially regarding the ductile behavior of the plastic, will be noted when 1 to 30 parts by weight of the diblock copolymer are utilized per 100 parts of the polyphenylene ether and polyamide components taken together.

As might be expected, lower amounts of the diblock copolymer modifier would achieve little useful effect, whereas excess amounts could detract from the physical properties of the thermoplastic resin composition. In preferred compositions, approximately 5 to 25 parts of the diblock copolymer modifier will be utilized per 100 parts by weight of the base resin.

The diblock copolymer rubber additive useful in compositions of the present invention is a thermoplastic rubber comprised of an alkenyl aromatic block which is typically a styrene block and an ethylene-propylene block which had been derived from a

- 15 -

partially or selectively hydrogenated block. These materials are commonly referred to as SEP diblocks. The weight ratio of the styrene block compared to the rubber block may be varied to a considerable degree and many useful compositions can be provided without difficulty. Typically, commercially available diblock copolymers having a styrene to rubber ratio of 20 to 40 parts styrene and 80 to 60 parts rubber will be preferred. These materials may be made by the anionic polymerization of the respective block components, followed by selective hydrogenation. Selective hydrogenation refers to the hydrogenation of some or all of the unsaturated sites on the rubber component as opposed to hydrogenation of the aromatic styrene component. This selective hydrogenation process is one feature which distinguishes SEP diblock from conventional SBR rubber compounds. The SEP diblock copolymers having selectively hydrogenated rubber blocks exhibit improved properties in compositions of the present invention, especially as compared to conventional non-hydrogenated diblock copolymers, as well as hydrogenated and non-hydrogenated triblock and multiblock copolymers.

Useful selectively hydrogenated diblock copolymers of the styrene-ethylene/propylene type are commercially available in a variety of grades from Shell Chemical Co. Commercial grades typically contain minor amounts of antioxidants and stabilizers. For purposes of the present disclosure it is intended that the selectively hydrogenated diblock copolymer of the styrene-ethylene/propylene type encompasses those similar diblock copolymers which may be provided from a variety of starting materials, in particular,

- 16 -

selectively hydrogenated diblock copolymers of styrene and isoprene.

5 The preparation of selectively hydrogenated block copolymers of alkenyl aromatic polymers and diene polymers is described in numerous patents, including U.S. 4,085,163 and 4,041,103 (both incorporated by reference) which also describe the use of such
10 ~~copolymers in polyamide resins. Their use in~~ compatible polyphenylene ether-polyamide resin systems was not foreseen nor was the improvement in such systems of the ductile behavior noted in the present invention.

The foregoing constituent ingredients can be compounded and molded by conventional means. The order of mixing and degree of shear experienced during
15 extrusion can be varied. It would be expected that the physical properties could vary as such processing conditions are varied. Those skilled in the art will be able to achieve optimum processing conditions which may vary for different thermoplastic applications.

20 Thus in one instance, each of the ingredients could be blended and extruded at once, thereby providing thermoplastic resin having a particular property profile. Alternatively it may be desirable to pre-blend or precompound some of the ingredients
25 while the remaining ingredients are charged later in a compounding or extrusion process.

In one embodiment, the polyphenylene ether, with or without a compatibilizing agent, could be pre-compounded with the diblock copolymer impact
30 modifier. Thereafter, the polyamide resin could be charged to the extruder downstream, at a point sufficient to provide adequate mixing but with minimum risk of degradation due to excess heat.

- 17 -

Additionally, it is expected that conventional additives such as fillers, pigments and flame retarding compounds and metal synergists can be incorporated in the thermoplastic compositions of the present invention, thereby providing a variety of useful products.

Unless otherwise noted, all formulations in the following examples are given in parts by weight. These examples should not be considered as limiting the scope of the invention in any way.

Examples 1 and 2

Several thermoplastic blends in accordance with the present invention were prepared and compared to compositions having conventional impact modifiers as described in Table 1. The polyphenylene ether was poly(2,6-dimethyl-1,4-phenylene ether) having an intrinsic viscosity of 0.45 as measured in chloroform at 25°C. The polyamide component was nylon 6, designated NYCOA 471 from Nylon Company of America. Except for two control blends, each blend in this series contained 50 parts by weight polyphenylene ether, 40 parts nylon 6, 0.5 parts of maleic anhydride compatibilizing agent, and 10 parts of the designated rubber additive.

The compositions were compounded by blending the requisite constituents which were extruded on a Werner & Pfleiderer 28 mm twin screw extruder having set temperatures over several stages of 450/530/535/540/550/560°F, no vacuum, at 280 rpm.

The compositions were molded on a Newbury three ounce injection molding machine having a barrel set temperature of 550-580°F, a mold set temperature of 150-160°F, and a total cycle time of 40 seconds. The

- 18 -

mode of failure in the Dynatup (DYN) falling dart impact test is characterized as B (brittle), B-D (brittle-ductile), or D (ductile) based on disk response to impact. Dynatup results are reported in 5 inch-pounds at maximum load (ML) and total energy (TE), at room temparture as well as -40°F.

TABLE 1

SAMPLE	RUBBER	MALEIC ANHYDRIDE	TEN. YLD. Kpsi	TUS Kpsi	TE %	IZOD ft. lbs./in. 66psi	HDT	DYN ML	DYN TE	MODE	FAILURE ML-40F	DYN TE-40F	FAILURE	FLOW CHANNEL(")
A*	none	none	6.8	6.8	5	0.8	367	7	12	B	B	11	B	23.5
B*	none	0.5	10.9	8.1	43	1.0	375	42	43	B	B	36	B	26.75
C*	SEBS triblock (a)	0.5	8.1	6.9	41	2.1	370	360	516	B-D	B	24	B	25.75
D*	SEBS triblock (b)	0.5	6.6	6.6	38	3.2	363	312	524	B	B	34	B	26.25
E*	SEBS triblock (c)	0.5	5.6	5.5	33	2.0	353	72	72	B	B	12	B	29
1	SEP diblock (d)	0.5	8.8	7.1	36	9.6	366	378	558	D	B	468	B	26.5
2	SEP diblock (e)	0.5	8.2	6.9	52	12.1	369	384	576	D	B	444	B	25.75
F*	SBS triblock (f)	0.5	8.2	7.2	72	7.1	365	408	583	D	B	492	B	25.25
G*	SBS triblock (g)	0.5	7.9	7.1	54	6.4	362	396	576	D	B	516	B	25
H*	SBS rubber (h)	0.5	9.0	7.4	52	4.5	351	348	538	D	B	444	B	26.75

* Samples A-H are comparative examples

(a) Kraton G 1651, Shell Chemical selectively hydrogenated styrene-ethylene/butylene-styrene triblock copolymer

(b) Kraton G 1652, Shell Chemical selectively hydrogenated styrene-ethylene/butylene-styrene triblock copolymer

(c) Kraton G 1657, Shell Chemical selectively hydrogenated styrene-ethylene/butylene-styrene triblock copolymer

(d) Kraton GX 1701, Shell Chemical, selectively hydrogenated styrene-ethylene/propylene diblock copolymer

styrene: rubber ratio is approximately 37:63

(e) Kraton GX 1702, Shell Chemical, selectively hydrogenated styrene-ethylene/propylene diblock copolymer

styrene:rubber ratio is approximately 27:73

(f) Kraton D 1101, Shell Chemical, styrene-butadiene-styrene triblock copolymer

(g) Kraton D 1102, Shell Chemical, styrene-butadiene-styrene triblock copolymer

(h) Stereon 840A, Firestone Chemical styrene-butadiene multiblock copolymer

- 20 -

It will be evident from the results reported in Table 1. that several physical properties of compatible polyphenylene ether-polyamide compositions can be improved upon the addition of the S-E/P diblock copolymer modifier utilized by the present invention.

Examples 3 and 4

In the following examples the polyphenylene oxide was melt extruded with a different polyamide, nylon-6,6 (Nylon Polymers NP 10,000). Distribution of the rubber in the resin matrix is an important requirement for good impact properties in polyphenylene ether-polyamide resins. In general it has been found that predispersing the rubber component in the polyphenylene oxide offers better typical properties. This may be accomplished by adding all of the rubber, compatibilizing agent, and the polyphenylene oxide to the throat of the extruder and splitting the nylon between the feedthroat and a downstream addition port. This downstream feeding is effective but requires extra equipment. It is often desirable to eliminate processing steps, where possible, from a manufacturing process.

In this series of experiments it can be seen that the SEP diblock rubbers give improved properties relative to conventional triblock rubbers without requiring downstream feeding of some of the nylon. The following blends were prepared using 49 parts polyphenylene oxide resin, 41 parts nylon 6,6, 10 parts of the rubber components, 0.50 parts maleic anhydride compatibilizing agent, 0.10 parts KI and 0.30 parts Irganox 1076 stabilizers. The blends were mixed in a Henshel mixer, extruded in a single pass on a 28mm Werner & Pfleiderer extruder and molded on a 3 ounce

- 21 -

Newbury molding machine. The extruder had a 550°F set temperature for most of the barrel, the molder was set at 550°F melt and 150°F mold. The physical properties were measured on standard ASTM parts. Results are

5 given in Table 2.

- 22 -

Table 2

Example	Rubber Type	Notch		Tensile		Dynatup		Mode of	
		Izod	Elongation	Impact	Failure				
3	Saturated SEP Diblock (a)	10.0	42	528	D				
4	Saturated SEP Diblock (a)	11.9	51	528	D				
I*	Unsaturated SBS Triblock (b)	4.8	89	456	D				
J*	Saturated SEBS Triblock (c)	6.6	62	600	D				
K*	Saturated SEBS Triblock (d)	2.1	41	204	B				

* Comparative Examples

(a) Kraton GX 1701

(b) Kraton D 1102

(c) Kraton G 1650

(d) Kraton G 1651

- 23 -

Examples 5-8

Blends were prepared as above using 24.5 parts polyphenylene ether, 24.5 parts PPO-TAAC compatibilizing agent, 41 parts nylon 6,6, and either 5 or 10 parts of the rubber component. The PPO-TAAC compatibilizing agent was the reaction product of a polyphenylene ether resin in solution and trimellitic anhydride acid chloride, which is thereafter isolated and dried. This PPO-TAAC compound is a functionalized polyphenylene ether, capable of compatibilizing a polyphenylene ether-polyamide composition and which, in this example, replaces 24.5 parts of the conventional polyphenylene ether. Table 3 describes the results where it can be seen that acceptable properties can be achieved with reduced rubber content, resulting in higher heat distortion values and lower costs. All modes of failure were of the ductile type.

-24-

Table 3

Example	Rubber Type (parts)	Notch Izod	Dynatup Impact	Tensile Elongation	HDT 66psi
M*	Unsaturated S-B-S (10) (a)	8.8	492	44	370
5	Saturated SEP diblock (10) (b)	10.4	552	67	387
6	Saturated SEP diblock (5) (b)	4.4	529	43	391
7	Saturated SEP diblock (10) (c)	9.8	551	53	381
8	Saturated SEP diblock (5) (c)	3.4	491	37	392

*Comparison

(a) Kraton D 1102 Triblock

(b) Kraton GX 1702 SEP diblock

(c) Kraton GX 1701 SEP diblock

- 25 -

Examples 9-12

Further blends were prepared, as above, using 0.70 parts citric acid as the compatibilizer in compositions containing 49 parts polyphenylene ether, 41 parts nylon 6,6 and between 5 to 15 parts of the rubber component. These blends contained 0.30 parts Inrganox 1076 and 0.10 parts KI stabilizers. These citric-acid based blends showed improvements using the SEP diblock in place of conventional triblock rubbers. In these blends the mode of failure was brittle.

- 26 -

Table 4

EXAMPLE	RUBBER TYPE (Parts)	NOTCH		DYNATUP	
		IZOD		IMPACT	
N*	Unsaturated SBS triblock (10) (a)	2.8		420	
9	Saturated SEP diblock (5) (b)	2.5		402	
10	Saturated SEP diblock (5) (b)	2.5		402	
11	Saturated SEP diblock (10) (b)	7.1		341	
12	Saturated SEP diblock (15) (b)	10.5		342	

* Comparison

(a) Kraton D 1102 triblock

(b) Kraton GX1702 SEP diblock

- 27 -

Examples 13

It has also been unexpectedly found that the saturated diblock rubbers utilized in the present invention provided excellent heat aging characteristics. This effect was not expected since previous work with saturated SEBS triblock rubber had shown no improvement in this regard. In these examples, 10 parts of the indicated rubber were used in polyphenylene ether-polyamide blends containing 49 parts PPE and 41 parts polyamide (Nylon 6,6), compatibilized with 0.7 parts citric acid. The SBS triblock rubber was Kraton D 1102 and the SEP saturated diblock rubber was Kraton GX1702. These blends contained 0.1 parts KI, 0.3 part Irganox 1076 hindered phenol, and 4 parts TiO_2 . Table 5 describes the results of this series of blends where mode of failure characterizations are given along with the Dynatup impact figures. In this series, B represents brittle failure, S represents a part which split upon impact indicating intermediate ductility.

- 28 -

TABLE 5

Example	Rubber Type	Initial N. Izod	Dynatup Impact (initial)			
			350°F 2 hr	350°F 4 hr	375°F 2 hr	325°F 4 hr
0*	SBS Unsatuated Triblock	2.8	480S	156S	144S	120B
13	SEP Saturated Diblock	7.1	480S	324S	456S	444S

- 29 -

Examples 14 to 17

Glass reinforced grades of compatibilized polyphenylene ether-polyamide blends are particularly useful in certain thermoplastic applications such as those requiring impact strength, dimensional stability or rigidity as well as chemical resistance. Such glass reinforced grades of compatibilized polyphenylene ether-polyamide blends can be improved in accordance with the present invention by incorporation of the selectively hydrogenated diblock copolymer of styrene and ethylene/propylene. Such glass reinforced PPE-PA blends are not only effectively impact modified by the diblock copolymer but, importantly, the blends exhibit much better retention of physical properties after heat aging of the samples. In the following examples, PPE-PA blends were compatibilized with either citric acid-1-hydrate or maleic anhydride and contained either 10 or 30 percent by weight of chopped glass fibers. The polymer mixtures were compounded on a 28 mm Werner & Pfleiderer twin screw extruder, all ingredients being added via a hopper at the feed throat. The extruder had a screw speed of 300 rpm, a temperature setting of 285°C, an output rate of 10 kg/hr, and a maximum vacuum of -1.0.

The 10% glass formulation was comprised of 42 parts by weight polyphenylene ether resin, 42 parts polyamide 6,6 resin, 10 parts chopped glass fiber, either 0.6 part citric acid-1-hydrate or 0.2 part maleic anhydride as compatibilizer, and 6 parts of the selected impact modifier. About 0.4 part of the total were the aforementioned stabilizers. The 30% glass formulation was prepared similarly but contained 27 parts by weight PPE resin, 37 parts polyamide 6,6

- 30 -

resin, 30 parts chopped glass fiber, either 0.5 part citric acid-1-hydrate or 0.2 part maleic anhydride compatibilizer, 0.3 part stabilizer and 6 parts impact modifier.

Table 6: Product performance of 10 and 30% glass filled PPE-polyamide blends with 6% impact modifier and citric acid-1-hydrate compatibilizer.

Mechanical Properties	(J/m)	10% Glass		30% Glass	
		P*	Q*	SBS Triblock (a)	SEP Diblock (b)
		SBS Triblock (a)	SEP Diblock (b)	SBS Triblock (a)	SEP Diblock (b)
Izod Impact	(J/m)				
- notched		105	98	99	103
- unnotched		> 1240	992	982	938
°40 hrs/air/180°C		278	755	390	714
°72 hrs/air/180°C		159	329	250	531
Tensile Strength (MPa)		73	74	98	98
°40 hrs/air/180°C		77	80	107	108
°72 hrs/air/180°C		65	80	104	106
Tensile Elongation (%)		21.9	8.8	7.3	4.7
°40 hrs/air 180°C		3.8	9.5	4.2	4.4
72 hrs/air 180°C		2.2	6.4	3.4	4.0
Tensile Modulus (MPa)		3300	3400	5750	6200
°40 hrs/air/180°C		3150	3500	6000	6550
°72 hrs/air/180°C		3250	3300	5700	5700
Flexural Strength (MPa)		115	121	158	161
Flexural Modulus (MPa)		2750	2900	4600	4850

* P and Q are comparative Examples

(a) SBS triblock: Cariflex TR-KX-65, Shell Chemical

(b) SEP diblock: Kraton GX 1701, Shell Chemical

Table 7: Product performance of 10 and 30% glass filled PPE-polyamide blends with 6% impact modifier and maleic anhydride compatibilizer.

Mechanical Properties	10% Glass		30% Glass	
	16		17	
	R*	SBS Triblock (a) SEP Diblock (b)	S*	SBS Triblock (a) SEP Diblock (b)
Izod Impact (J/m)				
- notched	125	143	137	156
- unnotched	1089	1018	1116	1175
°48 hrs/air/180°C	253	839	590	1100
Tensile Strength (MPa)	82	75	122	119
°48 hrs/air/180°C	83	81	136	132
Tensile Elongation (%)	15.0	11.2	5.3	4.8
°48 hrs/air 180°C	3.1	8.6	3.8	4.4
Tensile Modulus (MPa)	3600	3350	7150	6950
°48 hrs/air/180°C	3650	3400	7300	7050
Flexural Strength (MPa)	128	119	187	184
Flexural Modulus (MPa)	2700	2600	4950	4700

- 33 -

1. A thermoplastic composition having improved low temperature ductility comprising
 - A. 100 parts by weight of a base resin comprising a compatibilized polyphenylene ether resin and polyamide resin, and
 - B. 1 to 30 parts by weight of a selectively hydrogenated diblock copolymer of the A-B type wherein block A is an alkenyl aromatic polymer and block B is an ethylene-propylene polymer.
2. A composition as in Claim 1 wherein said compatible base resin is comprised of (a.) 5 to 95 weight percent polyphenylene ether resin and (b.) 95 to 5 weight percent polyamide resin, based upon the weight of a. and b. together.
3. A composition as in Claim 2 wherein said polyamide resin constitutes a continuous phase in an amount greater than, approximately, 35 weight percent of the resinous components.
4. A composition as in Claim 1 further comprising a compatibilizing agent selected from the group consisting of: maleic anhydride, fumaric acid, citric acid, malic acid, and reaction products of a polyphenylene ether and trimellitic anhydride acid chloride.
5. A composition as in Claim 1 wherein said polyphenylene ether resin is a polymer or copolymer comprised primarily of one or more units derived from units selected from the group consisting of 2,6-dimethyl phenol units and 2,3,6-trimethyl phenol

- 34 -

units, and wherein said resin has an intrinsic viscosity of 0.25 to 0.6 dl/g as measured in chloroform at 25°C.

6. A composition as in Claim 5 wherein said polyphenylene ether is poly(2,6-dimethyl-1,4-phenylene ether).
7. A composition as in Claim 1 wherein said polyamide resin is selected from the group consisting of polyamide 6, and polyamide 6,6.
8. A composition as in Claim 1 wherein said diblock copolymer is comprised of, approximately, 20 to 40 weight percent styrene and 80 to 60 weight percent ethylene-propylene polymer based upon the weight of both blocks taken together.
9. A composition as in Claim 1 wherein said diblock copolymer comprises, approximately, 5 to 25 parts by weight based upon the total weight of polyphenylene ether and polyamide.
10. A composition as in Claim 1, further comprising (C.) a reinforcing amount of glass fibers.
11. A composition as in Claim 10 wherein the glass fibers are present in an amount of, approximately, 5 to 45 weight percent based upon the weight of components A., B., and C. taken together.
12. A method for improving the ductile behavior of a polyphenylene ether-polyamide composition, comprising the steps of:
 providing a compatible polyphenylene ether polyamide base resin comprised of at least 35 weight percent polyamide resin based upon the weight of all resinous components taken together and an amount of a compatibilizing agent effective for facilitating a

- 35 -

continuous phase of polyamide in said polyphenylene ether-polyamide base resin;

compounding together with said compatible polyphenylene ether-polyamide base resin a ductile property improving amount of a selectively hydrogenated diblock copolymer comprised of an alkenyl aromatic polymer block and an ethylene/propylene block, thereby providing an improved polyphenylene ether-polyamide composition.

- 13.A method as in Claim 12 further comprising the step of extruding said polyphenylene ether-polyamide compositions in a thermoplastic extruder to provide a thoroughly uniform and compatible resin composition.
- 14.A method as in Claim 13 further comprising the step of pelletizing said extrudate to provide a uniform resin product.
- 15.A method as in Claim 14 further comprising the step of injection molding said resin product to provide a thermoplastic article of manufacture.
- 16.A method as in Claim 12 wherein said diblock copolymer is comprised of a styrene block and an ethylene/propylene block and the weight ratio of styrene to rubber is, approximately, 20 to 40 parts styrene and 80 to 60 parts rubber.
- 17.A method as in Claim 16 wherein said selectively hydrogenated diblock copolymer is utilized in an amount of, approximately, 1 to 30 parts by weight based upon the weight of the polyphenylene ether and polyamide.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 87/00479

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 08 L 71/04; C 08 L 77/00; C 08 L 53/00																				
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black; padding: 5px;">Classification System</td> <td style="border-bottom: 1px solid black; padding: 5px;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁴</td> <td style="padding: 5px;">C 08 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div>			Classification System	Classification Symbols	IPC ⁴	C 08 L														
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III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%; padding: 5px;">Category ¹⁰</th> <th style="width: 70%; padding: 5px;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; padding: 5px;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">WO, A, 85/05372 (GEN. ELECTRIC) 5 December 1985 see claims; page 14, lines 11-35; page 15, lines 1-33 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0046040 (ASAHI-DOW) 17 February 1982 see claims --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0024120 (SUMITOMO) 25 February 1981 see claims --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;">EP, A, 0142166 (MONTEDISON) 22 May 1985 see claims; page 4 --</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">E</td> <td style="padding: 5px;">WO, A, 87/00540 (GEN. ELECTRIC) 29 January 1987 see claims; page 12, lines 1-14 -----</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	WO, A, 85/05372 (GEN. ELECTRIC) 5 December 1985 see claims; page 14, lines 11-35; page 15, lines 1-33 --	1	A	EP, A, 0046040 (ASAHI-DOW) 17 February 1982 see claims --	1	A	EP, A, 0024120 (SUMITOMO) 25 February 1981 see claims --	1	A	EP, A, 0142166 (MONTEDISON) 22 May 1985 see claims; page 4 --	1-17	E	WO, A, 87/00540 (GEN. ELECTRIC) 29 January 1987 see claims; page 12, lines 1-14 -----	1
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INTERNATIONAL APPLICATION NO.

PCT/US 87/00479 (SA 16539)

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 8505372	05/12/85	AU-A- 4409985 EP-A- 0185054 JP-T- 61502195	13/12/85 25/06/86 02/10/86
EP-A- 0046040	17/02/82	JP-A- 57036150 US-A- 4339376 AU-A- 7401981 AU-B- 526692 CA-A- 1166389 JP-A- 57065750	26/02/82 13/07/82 06/05/82 27/01/83 24/04/84 21/04/82
EP-A- 0024120	25/02/81	JP-A- 56026913 US-A- 4315086 CA-A- 1155583 JP-A- 56047432 JP-A- 57010642	16/03/81 09/02/82 18/10/83 30/04/81 20/01/82
EP-A- 0142166	22/05/85	JP-A- 60118739	26/06/85
WO-A- 8700540	29/01/87	AU-A- 6199686 NL-A- 8502116	10/02/87 16/02/87

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